Like likes like in ionic liquids: When cooperative hydrogen bonding overcomes Coulomb repulsion between ions of like charge

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Abstract

"Unlike charges attract, but like charges repel". This conventional wisdom has been recently challenged for ionic liquids (ILs). Here we show that like-charged ions attract each other despite the powerful opposing electrostatic forces. In principle, cooperative hydrogen bonding between ions of like-charge can overcome the repulsive Coulomb interaction while pushing the limits of chemical bonding. The key challenge of this solvation phenomenon is to establish design principles for the efficient formation of clusters of like-charged ions in ionic liquids. For that purpose, we combined weakly coordinating anions with polarizable cations, which are all equipped with hydroxyl groups for possible H-bonding. The formation of H-bonded cationic clusters can be controlled by the interaction strengths of the counterions and the delocalization of the positive charge on the cations. Strongly interacting anions and localized charges on the cations result in hydrogen bonded ions of opposite charge, whereas weakly coordinating anions and delocalized charge on the cations lead to the formation of H-bonded cationic clusters up to cyclic tetramers. If we increase the distance between the hydroxyl groups and the positive charge centre on the cation we can further support the cationic cluster formation. These clusters are observed by bulk infrared (FT-IR) and cryogenic vibrational spectroscopy, and interpreted by density functional theory (DFT) calculations on neutral and ionic clusters. The formation of cationic clusters is also reflected in the NMR proton chemical shifts and in the rotational correlation times of the OH groups. Additional molecular dynamics simulations (MD) provide information about the lifetimes of the hydrogen bonds in the cationic clusters compared to those in the typical ion pairs.